Investigation of unoccupied electronic states of LaCoO$_3$ and PrCoO$_3$ using inverse photoemission spectroscopy and GGA $+ U$ calculations

S. K. Pandey,[1] Ashwani Kumar,[2] S. Banik,[1] A. K. Shukla,[1] S. R. Barman[1] and A. V. Pimpale[1]

[1] *UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 017, India.*
[2] *Department of Physics, Institute of Science and Laboratory Education, IPS Academy, Indore 452 012, India.*

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The unoccupied electronic states of LaCoO$_3$ and PrCoO$_3$ are studied using room temperature inverse photoemission spectroscopy and *ab initio* GGA+U band structure calculations. A fairly good agreement between experiment and theory is obtained. The intensity of the peak just above the Fermi-level is found to be very much sensitive to the hybridization of Co 3d and O 2p orbitals. Moreover, the band just above the Fermi-level is of Co 3d character with little contribution from O 2p states.

Perovskite type transition metal oxides with general formula ABO$_3$ (A $\equiv$ rare-earth ions and B $\equiv$ transition metal ions) have been of much interest for more than fifty years.[1] Recently, research activities have been intensified in this class of materials due to the emergence of exotic properties like charge-disproportionation, charge ordering, orbital ordering, phase separation, colossal magneto resistance *etc.*[1] The interplay between the on-site and inter-site Coulomb interaction, the charge transfer energy, the hybridization strength between the cation 3d and oxygen 2p states and the crystal field splitting for the $d^n p^m$ configuration of the BO$_6$ octahedron control the ground state electronic structure and magnetic and transport properties of these perovskites.

Cobaltates with general formula ACoO$_3$ forms an interesting class of compounds in the perovskite family. The ground states of these compounds are believed to be nonmagnetic (spin S = 0) insulator having Co^{3+} ion in the low spin configuration with fully filled Co t_{2g} orbitals. These compounds show insulator to metal and non-magnetic to paramagnetic transitions with increase in temperature.[2,3,4,5,6] It is believed that such transition occurs due to thermally driven spin state transition of Co^{3+} ion.[7,8,9] To understand the electronic transport in these compounds the understanding of both the occupied and the unoccupied electronic states is desirable. Most of the work found in literature deals only with occupied part of the electronic states.[10,11,12,13,14,15,16] There are very few reports in the literature dealing with the unoccupied electronic states and most of them are based on x-ray absorption studies of LaCoO$_3$.[17,18,19]

Here we study the unoccupied electronic states of LaCoO$_3$ and PrCoO$_3$ using inverse photoemission spectroscopy (IPES) and show how the unoccupied electronic states is affected when La is replaced by Pr. The replacement of La by Pr has two fold effect: (i) change in chemical pressure due to changed ionic radius and (ii) change in the electronic occupancy of 4f states. The change in chemical pressure may affect the crystal structure of PrCoO$_3$. The powder diffraction work has shown the crystal structure of LaCoO$_3$ and PrCoO$_3$ as rhombohedral and orthorhombic, respectively.[6,20] The Pr^{3+} ion

contains two electrons in the 4f states. This would contribute to the valence band and expected to affect the unoccupied electronic structure of the compound.

In the present work, we investigate the room temperature unoccupied electronic structure of LaCoO$_3$ and PrCoO$_3$ compounds using IPES and *ab initio* band structure calculation. The comparison of experimental spectra with the convoluted total density of states indicates that GGA+U calculation is sufficient for understanding all experimentally observed features in the spectrum. On going from LaCoO$_3$ to PrCoO$_3$ intensity of peak just above the Fermi-level decreases for PrCoO$_3$ due to decrease in the hybridization of Co 3d and O 2p orbitals in this compound in comparison to LaCoO$_3$. The band just above the Fermi-level is of Co 3d character.

LaCoO$_3$ and PrCoO$_3$ were prepared in the polycrystalline form by combustion method.[21] Nitrates of La, Pr and Co were taken in appropriate amount and mixed in double distilled water. In this mixture, 2 moles of glycine per 1 mole of metal cation was added and stirred until all the compounds dissolved in the water. The resulting solution was heated slowly at temperature around 200^{0}C till all the water evaporated. The precursor thus formed catches fire on its own making the powder of the desired compound. The hard pellets of this powder were formed and heated at 1200^{0}C for one day. The samples were characterized by x-ray powder diffraction technique. The powder diffraction data did not show any impurity peak; all the peaks of LaCoO$_3$ and PrCoO$_3$ were well fitted with rhombohedral (space group $R\overline{3}c$) and orthorhombic (space group $Pbnm$) phases, respectively, using Rietveld refinement technique. The lattice parameters obtained from the fitting match well with those reported in the literature.

The inverse photoemission spectroscopy experiments on LaCoO$_3$ and PrCoO$_3$ compounds were performed under ultrahigh vacuum at a base pressure of 6 $\times$ 10^{-11} mbar. The samples were mounted in the form of a compressed hard pellet and they were scraped uniformly by diamond file to obtained clean surface. An electrostatically focused electron gun of Stoffel Johnson design and an acetone gas filled photon detector with a CaF$_2$ window

were used for the experiments.[22,23] The experiments were carried out in the isochromat mode where the kinetic energy of the incident electrons were varied at 0.05 eV steps and photons of fixed energy (9.9 eV) were detected with an overall resolution of 0.55 eV.[23] Fermi-level was aligned by recording the IPES spectrum of *in situ* cleaned silver foil.

The GGA+U spin-polarized density of states (DOS) calculations of LaCoO$_3$ were carried out using LMTART 6.61.[24] For calculating charge density, full-potential linearized Muffin-Tin orbital method working in plane wave representation was employed. In the calculation, we have used the Muffin-Tin radii of 3.509, 2.001, and 1.674 a.u. for La, Co and O, respectively. The charge density and effective potential were expanded in spherical harmonics up to $l=6$ inside the sphere and in a Fourier series in the interstitial region. The initial basis set included $6s$, $6p$, $5d$, and $4f$ valence, and $5s$ and $5p$ semicore orbitals of La; $4s$, $4p$, and $3d$ valence, and $3p$ semicore orbitals of Co, and $2s$ and $2p$ valence orbitals of O. The exchange correlation functional of the density functional theory was taken after Vosko *et al.*[25] and generalized gradient approximation (GGA) was implemented using Perdew *et al.* prescription.[26] In the GGA+U calculations the Hubbard U and exchange J are considered as parameters. We have taken $U=3.5$ eV and $J=1.0$ eV for Co $3d$ electrons. The values of U and J for $3d$ electrons are consistent with our previous studies.[13,15] Self-consistency was achieved by demanding the convergence of the total energy to be smaller than 10^{-5} Ryd/cell. (6, 6, 6) divisions of the Brillouin zone along three directions for the tetrahedron integration were used to calculate the density of states.

The experimental spectra of LaCoO$_3$ and PrCoO$_3$ are plotted in Fig. 1. The normalized spectra of these compounds in the region closer to Fermi-level are given in the inset of the figure. Three features are clearly seen in the spectrum corresponding to LaCoO$_3$ denoted by A, B and C. Peak B is not visible in the PrCoO$_3$ spectrum. It may be noted that the first peak A is somewhat more asymmetric for lanthanum compound as compared to praseodymium one. This may be an indication of some additional structure around this energy in LaCoO$_3$. The feature B is not seen in the bremsstrahlung isochromat spectroscopy (BIS) data of LaCoO$_3$ of Chainani *et al.*[18] This may be due to different cross-section and worse resolution of the BIS data. It is clear from the inset that there is little intensity near the Fermi-level taken as energy origin indicating the insulating nature of the compounds. One may note the rise in the intensity above the Fermi-level, which is relatively sharper for LaCoO$_3$ in comparison to PrCoO$_3$. Also the height of peak A corresponding to PrCoO$_3$ is less in comparison to that in LaCoO$_3$.

The experimental and calculated spectra of LaCoO$_3$ are plotted in Fig. 2. The calculated spectrum also contains three features denoted by arrows corresponding to experimentally observed features A, B and C. In addition a structure is seen around 3 eV, which may account for

the asymmetry of the peak A in the experimental data. There is some deviation in the energy positions and the corresponding intensities of the features. Such deviation may be due to approximations involved in the calculations. It should be mentioned here that our calculations of IPES is based only on total DOS and matrix element as well as inelastic background are not considered. Keeping this in mind, the agreement between experiment and calculation as far as features are concerned is reasonably satisfactory.

To identify the contribution of different partial DOS in different features, we have plotted the Co $3d$, O $2p$, La $5d$ and La $4f$ partial DOS in Fig. 3 as these DOS contribute most in the energy regions of interest. It is evident from the panels 1 and 2 that in feature A, Co $3d$ and O $2p$ states contribute. There is a substantial rise in Co $3d$ DOS just above the Fermi level indicating that the region just above it has only Co $3d$ character. Feature B mainly arises from electronic transition to mixed La $5d$ and La $4f$ states. The feature C can be attributed to mixed O $2p$, La $5d$ and La $4f$ states. It is evident from panels 2, 3 and 4 that the La $4f$ partial DOS is much larger than the O $2p$ and La $5d$ partial DOS. Therefore, any change in the number of electrons in the $4f$ orbital will have direct effect on the intensity of features B and C. This is clearly evident from figure 1 where the intensity of these features decreases for PrCoO$_3$ in comparison to LaCoO$_3$. In PrCoO$_3$ there are two electrons in the occupied $4f$ band, whereas in LaCoO$_3$ the $4f$ band is fully unoccupied. Thus one expects a decrease in the intensity of features having $4f$ character (in the case of PrCoO$_3$) and this is clearly seen in the data. The reduced asymmetry and intensity under peak A for PrCoO$_3$ can be seen to be due to unoccupied O $2p$ DOS. It may be noted that the overlap of Co $3d$ and O $2p$ orbitals is some what reduced for the PrCoO$_3$ in comparison to LaCoO$_3$ due to increased average Co-O bond length as revealed by our extended x-ray absorption fine structure (EXAFS) studies.[27] The decrease in overlap will reduce the transfer of electron from O $2p$ to Co $3d$ orbital and as a consequence decrease in unoccupied O $2p$ band. The interpretation is in line with the plotted partial DOS in panel 2 of figure 3 where O $2p$ DOS contributing to these features is 1 eV above the Fermi-level from where the intensity started decreasing for PrCoO$_3$, as is evident from Fig. 1. This behaviour of intensity clearly indicates that the band just above the Fermi-level is of d character arising from Co $3d$ partial DOS. This result is in contrast with configuration interaction calculations of Saitoh *et al.*[28] giving O $2p$ character of band just above the Fermi-level for LaCoO$_3$.

In conclusion, we have carried out room temperature inverse photoemission spectroscopy (IPES) measurements on LaCoO$_3$ and PrCoO$_3$ compounds. The IPES data are analyzed by using density of states obtained from GGA+U calculation. It is noted that such calculations might suffice to understand the features observed in the experimental spectra up to 12 eV above the Fermi-

level. The hybridization of Co $3d$ and O $2p$ orbitals is found to be crucial for understanding the change in intensity of the peak just above the Fermi-level. The band just above it is of Co $3d$ character with little contribution from O $2p$ states.

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I. FIGURE CAPTIONS:

Fig. 1: (color online) Inverse photoemission spectra of $LaCoO_3$ and $PrCoO_3$. Inset shows the normalized spectra near the Fermi-level of these compounds. The energy origin is taken at the Fermi-level.

Fig. 2: (color online) The experimental and calculated inverse photoemission spectra of $LaCoO_3$.

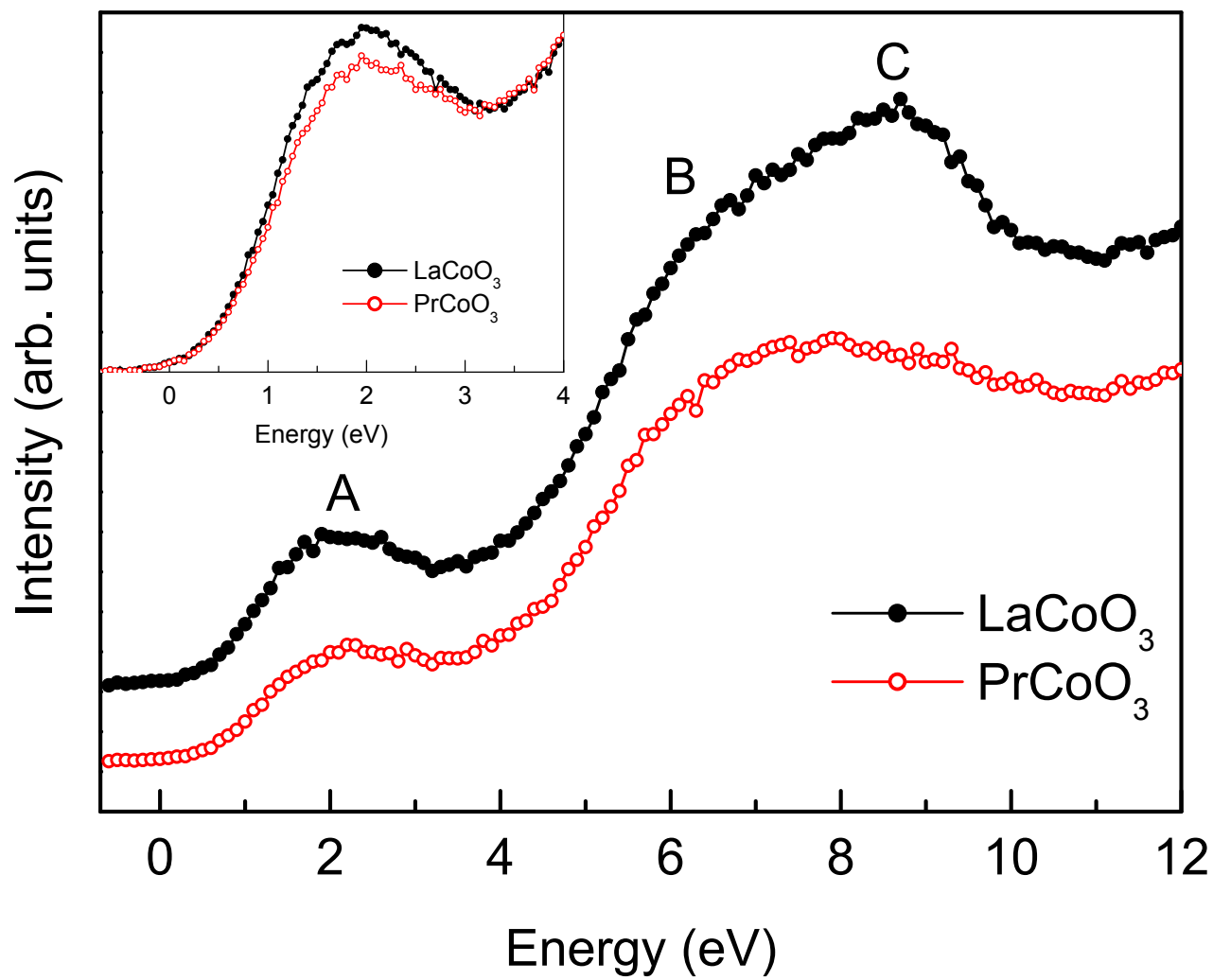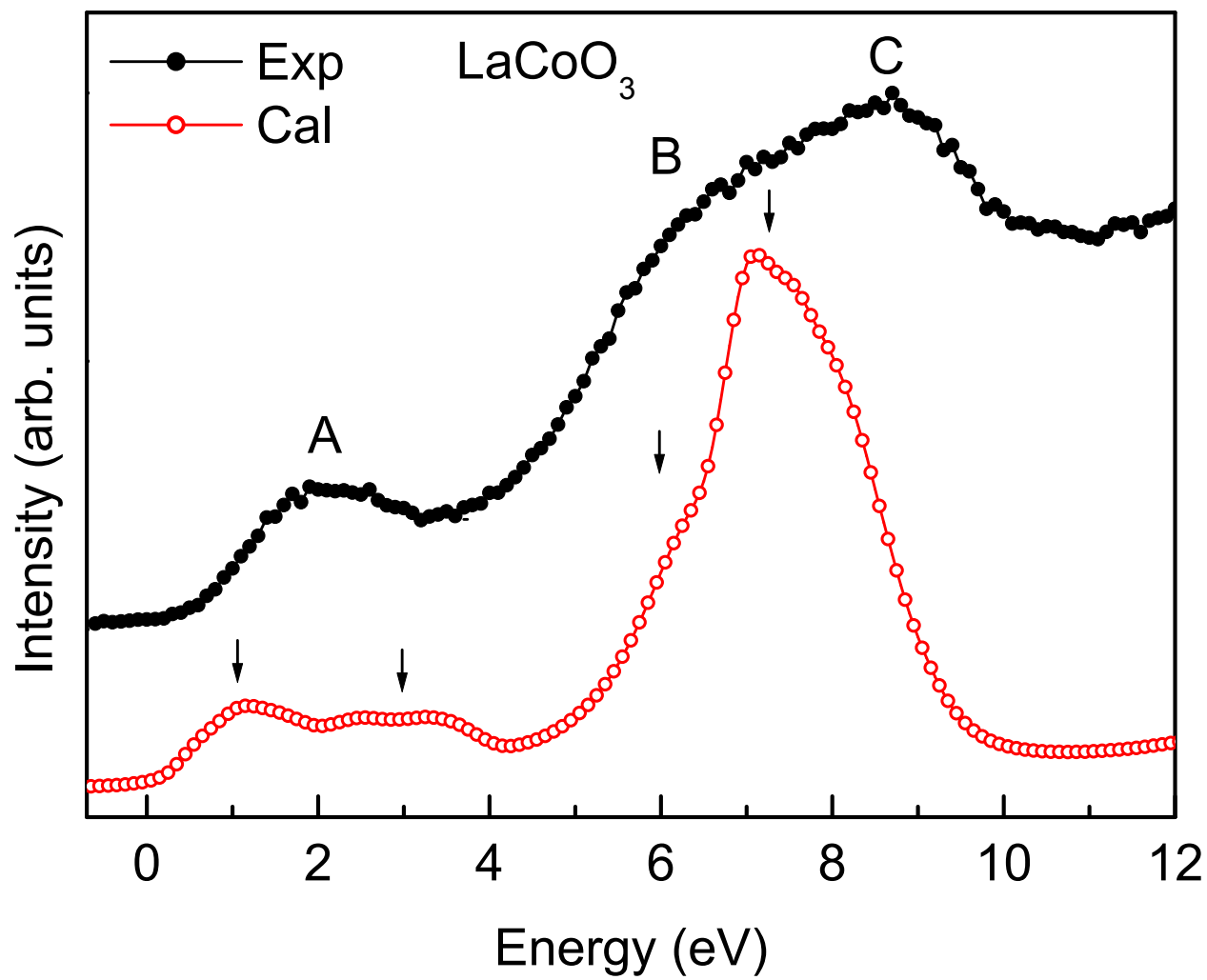Fig. 3: Partial density of states of Co $3d$, O $2p$, La $5d$ and La $4f$ characters.

Fig. 1
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Fig. 2
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Fig. 3
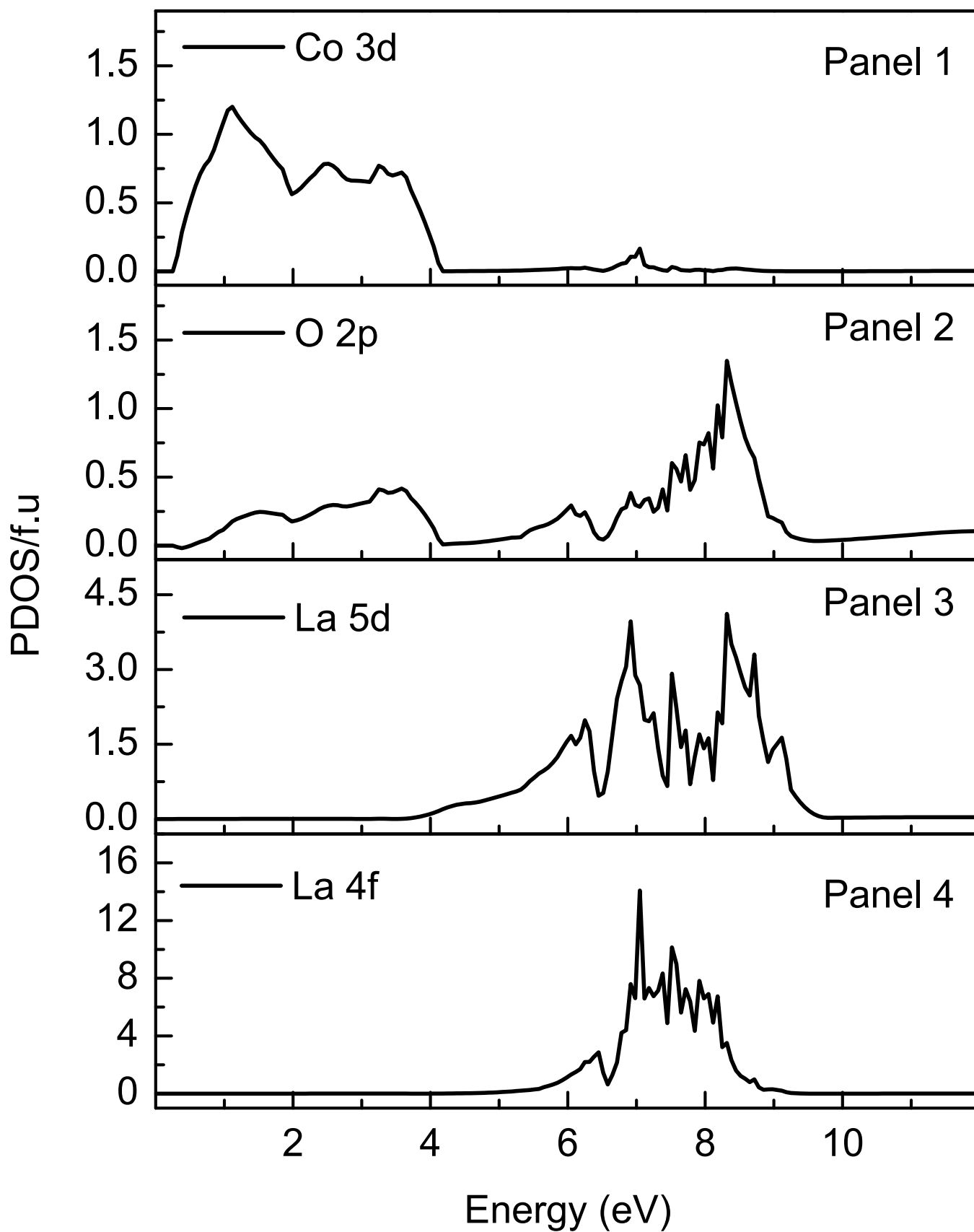Pandey et al.